REPORT DOCUMENTATION PAGE

AD-A255 977

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	8-24-92	Final 3/15/92 - 8/31/92

4. TITLE AND SUBTITLE

Organization of Workshop on Emerging Technologies for In-Situ Processing

5. FUNDING NUMBERS

F49620-92-J-0233

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

AFOSR-TR- 92 0818

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Office of Scientific Research
Bldg. 410,
Bolling Air Force Base, DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

2301/FS

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

DTIC ELECTE OCT 07 1992 S A D

13. ABSTRACT *(Maximum 200 words)*

Work by Dr. Melngailis and his collaborators is summarized here

92 10 6 056

92-26575

78 pgs

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Final Report to

Air Force Office of Scientific Research

for

Organization of Workshop on
Emerging Technologies for In-Situ Processing

for the period March 15, 1992 to August 31, 1992

submitted to

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AFOSR/Physics
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submitted by

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Massachusetts Institute of Technology
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Cambridge, MA 02139

Advanced Research Workshop on *In situ* Processing

Viana do Castelo, Portugal

26 April - 2 May 1992

The goal of the workshop was to bring together government, industrial and university representatives to assess the progress and future direction of in *situ* processing of semiconductors.

Since the first NATO Workshop in this topic area (Cargese, Corsica in 1987) there has been surprising progress toward the industrial applications, particularly as exemplified by cluster tools and laser/ion beam real-time fabrication machines. There remains an obvious communications gap between the industry, which is eager to accept this technology and the research community, which only partially understands the industry motivations and needs. The Government Agencies are actively working to bridge this gap and to provide a focus for longer-term development.

The consensus of the workshop was that the economic implications of *in situ* processing are accelerating strongly, particularly for smaller countries (or even larger ones) where the costs of traditional semiconductor factories are growing at unacceptable rates. This problem and the potential solutions were the central themes of the conference. The talks by Larrabee, Saraswat and Prabhakar pointed to the need for future factories that are smaller and use flexible intelligent manufacturing. In semiconductor device manufacturing, in particular, smaller lots, cluster tools (i.e. in-situ processing), and tight process control will result in better contamination control and lower cost. The other talks of the conference provided specific examples of advances in in-situ processing that will contribute to making this vision of intelligent flexible manufacturing a reality.

The relative novelty of *in situ* processing, however, is outside the mainstream experience of the industry, and there is great opportunity for the university research community to contribute major parts of the new technology. Important information was

exchanged between university and industrial researchers and communications between these groups will help significantly to make both more productive. The accelerating pace of development in *in situ* processing suggests that there is need to follow-up the topic area, and to enhance the industrial representation in a third workshop in approximately 2 years time.

The amount awarded was expended, as budgeted, to support the travel costs of invited US participatns. Details are below.

A program and book of abstracts also accompanies this report.

Financial Statement

Award Amount	$10,000

Expenditures:

Travel expenses for:

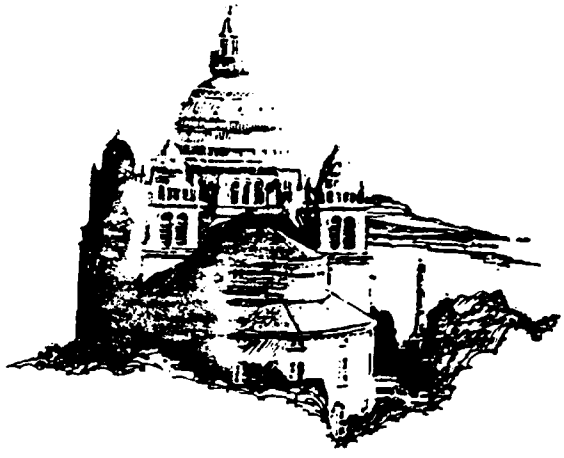
- Steve Holmes (IBM)	$ 500
- John Lankard (IBM)	$ 200
- G. Lucovsky (NC State)	$ 400
- Steve Brueck (U. New Mexico)	$ 750
- Krishna Saraswat (Stanford)	$ 750
- Henry Helvajian (Aerospace Corp.)	$ 500
- Lloyd Harriott (Bell Labs)	$ 500
- Jon Orloff (Oregon Grad. Inst.)	$ 750
- Tom Sigmon (Oregon Grad. Inst.)	$ 750
- Susan Allen (Iowa State)	$ 750
- Sanjay Banerjee (U. Texas Austin)	$ 300
- Dan Ehrlich (Lincoln Lab)	$ 465
- John Melngailis (MIT)	$ 460
- Registration for the above 13 participants at $225 each	$2,925
Total	$10,000

NATO ASI WORKSHOP ON IN SITU PROCESSING

THE PHYSICS AND TECHNOLOGY OF SURFACE MODIFICATION

VIANA DO CASTELO, PORTUGAL
27 APRIL-1 MAY 1992

TECHNICAL PROGRAM



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SUPPLIMENTAL SUPPORT: DARPA

NATO ASI WORKSHOP ON IN SITU PROCESSING
PROGRAM

Mon. 27 April

SESSION 1 - INTEGRATED PROCESSING I
(Chairs: I. Boyd, V. T. Nguyen)

8:20 AM	Chairmans Remarks
Graydon Larrabee	Manufacturing Issues Driving In Situ Processing
Krishna Saraswat	Microfactories with Multiprocessing Equipment for IC Manufacturing
Gerry Lucovsky	A Novel Two-Step, Low-Temperature, Plasma-Assisted Surface Oxidation/Thin Film Deposition Process
10:20 AM	(Coffee)
Steve Holmes	In Situ Process Control Opportunities for a Deep UV Photolithography Cluster
C. Licoppe	UV Treatment of Native Oxides With Silane
Steve Brueck	Real-Time Process Monitors for In Situ Processing
	(Discussion: Lemnios)

SESSION 2 - INTEGRATED PROCESSING II
(Chairs: Z. Lemnios, S. Brueck)

1:30 PM	
Ron Lawes	Future Issues with Lithography
Atilla Aydinli	Pulsed Laser Deposition of Some II-VI Alloys
Robert Jackman	In Situ Processing of GaAs With Photons
3:30 PM	(Coffee)
Minot Green	Recent Work on Novel Processing
Gabriel Crean	Optical Diagnostic Techniques for Fabrication Process Technologies
Dan Ehrlich	Room-Temperature CVD Without a Plasma
	(Discussion: Larrabee)

Tues. 28 April

SESSION 3 - REAL-TIME PROCESSING
(Chairs: D. Ehrlich, J. Orloff)

8:20 AM

Arati Prahakar	Flexible Intelligent Microelectronics Manufacturing
John Lankard Sr.	Laser-Based Tools in IBM's Manufacturing Lines
Peter Roberts	The Thermolytic LCVD of High Purity Gold Tracks from Alkyl Trialkyl Phosphine Gold (x) Complexes
	(Coffee)

10:20 AM

Geoffroy Auvert	Applications of Laser and Ion Beam Processing in The Repair of Integrated Circuits
B. Wolff-Rottke	Excimer Laser Micromachining
Chris Talbot	5-Year Projection for Commercialization of Beam Technologies in Circuit Engineering and Testing
	(Discussion: Lankard)

SESSION 4 - BEAM PROCESSING I
(Chairs: A. Prabhakar, T. Sigmon)

1:30 PM

Michael Stuke	Laser Materials Processing by Ablation and Deposition
Peter Dyer	Laser Ablation Deposition of Thin Films
Fransesco Fuso	Laser Ablation Deposition of Thin Films and surface Analysis by STM/AFM
	(Coffee)

3:30 PM

Henry Helvajian	Laser Material Interaction for Atomic Layer Processing
Herman Maj	A Modified Plasma Source for Controlled Layer Thickness Synthesis
Dolores Fernandez	Total Pressure and Substrate Temperature Dependence of the CO_2 Laser-Induced CVD of Silica Films
Didier Tonneau	Laser Induced Deposition of Aluminum From Trimethylamine/Alane
	(Discussion: Stuke)

Wed. 29 April

SESSION 5 - BEAM PROCESSING II
(Chairs: J. Melngailis, S. Namba)

8:20 AM	
Lloyd Harriot	Vacuum Lithography for In Situ Nanostructure Fabrication using Finely Focused Ion Beams and Molecular Beam Epitaxy
Kam Leung Lee	Direct E-Beam Deposition of 3 Dimensional Nanometer-Scale Atomic Force Microscope
Jon Orloff	Emerging Applications of Focused Ion Beams
	(Coffee)
10:20 AM	
Tomonori Ishikawa	In-Situ E-Beam Lithography of GaAs for Nanometer-scale Structures
Kengi Gamo	Low Energy Fused Ion Beam System and In Situ Processing
Mikio Takai	Nanofabrication Using STM Tip
	(Discussion: Melngailis)

Thur. 30 April

SESSION 6 - SURFACE PREPARATION
(Chairs: L. Vidigal, M.Stuke)

8:20 AM

Thomas Sigmon	Doping of Silicon using Pulsed Laser Techniques
Susan Allen	Dry Cleaning Methods for Semiconductor and Other Critical Surfaces
Jean Flicstein	UV-Induced Removal of Hydrogen, Hydroxyl and Water Groups in Silica Thin Films Photodeposited at Low Temperatures
	(Coffee)

10:20 PM

Werner Zapka	Laser Cleaning of Surfaces
J. Boulmer	Laser-assisted etching of silicon by Chlorine: Progress of a mechanistic study
Hiroshi Kumagai	Periodic Submicron Dot Structures on Semiconductor Substrates Fabricated by Laser-Induced Surface Electromagnetic Wave Etching
	(Discussion: Lucovsky)

SESSION 7 - MONITORS AND CONTROLS
(Chairs: R. Elliatioglu, P. Dyer)

1:30 AM

Walter Lowe	Synchrotron Radiation as an in-situ monitoring and Processing Tool
Carmen Afonso	Real Time Plume Diagnostics During Laser Ablation in an Oxygen Atmosphere
Sanjay Banerjee	Laser and Remote Plasma-enhanced Low Temperature Si and Si-Ge Epitaxy
	(Coffee)

3:30 PM

Wladimiz Marine	Dynamics of YO Monoxide Formation during YBCO Laser Ablation
James Lunney	Ion Emission Studies of Pulsed Laser Deposition
Gerd Maidorn	Optical Characterization of Metal Contamination in Silicon via Femtosecond Pulses
G. Tyrrell	Kinetic Energy and Mass Distributions of Ablated Species formed during Pulsed Laser Deposition
	(Discussion: Mair)

Fri. 1 May

SESSION 8 - BEAM PROCESSING III
(Chairs: R. Lawes, M. Green)

8:20 AM	
Gerard Pelous	Applications of Local Laser CVD in Microelectronics
John Whitney	Focused Ion Beams for Device Modification
Michel Meunier	Laser Assisted Deposition of Tungsten Lines and Columns on Silicon Oxynitride: Process Characterization and Applications
Claudio Arnone	Laser Direct Writing of Gold Conductors from Metallo-organic Inks
Mario Bertolotti	Laser and Thermal Processing for Ti:$LiNbO_3$ Waveguides
	(Coffee)
10:20 AM	
P. Gonzales	ArF Laser CVD Silicon Oxide Films Tailored by Tuning Gas-Phase Parameters
F. Sanchez	Ceramic Thin Films Deposited on Si (100) by Laser Ablation
Patrick Desjardins	Diode Laser Induced Chemical Vapor Deposition of WSi_x on TiN From WF_6 and SiH_4
1:30 PM	POSTDEADLINE SESSION
	(TBD)
	(Discussion: Co-Chairmen)

MANUFACTURING CHALLENGES FOR IN SITU PROCESSING

Graydon B. Larrabee
Booz-Allen & Hamilton

The 1990's will see dramatic changes in microelectronics manufacturing. These changes are being driven by technical challenges:

Wafer diameter	150mm -> 200mm -> 300mm
Minimum feature size	0.5 μm -> 0.35 μm -> 0.25 μm
Killing defect size	1000 Å -> 700 Å -> 500 Å
Chip size	140 mm^2 -> 200 mm^2 ->300 mm^2
Numbers of mask levels	20 -> 24 -> 28
Wafer fab costs	$600M -> $900M -> $1300M

In situ processing offers solutions to many of these technical challenges. It also presents manufacturing challenges that must be solved if situ processing is to be successful.

To many, in situ processing is synonymous with vacuum processing. The new cluster tools are predominantly vacuum equipment. Sources of particles will continue to be equipment and processes (not the cleanroom or people). In situ processes must be particle-free. This implies a new ultraclean technology with a new infrastructure. Liquids must be eliminated from processing chemistries. Point-of-use gas generation, filtration, purification and disposal are required.

Mini environments will be necessary to move wafers between equipment clusters. Interface engineering will be needed to support this mini environment technology. Surface chemistry will play an ever increasing role to protect the interface. Here again, liquids must be eliminated. It will also be necessary to eliminate off-line process control.

Real time process control, as practiced in the chemical industry, is essential for robust in situ manufacturing. Current Cp and Cp_k values are near 1.0 in our industry. They must be driven to 2.0 or greater for in situ manufacturing in the late 1990's. Real time process control will make this happen because it drives process reproducibility (Cp) and drives the process to the target value (Cp_k). It supports the requirement that the wafer never leaves the in situ processing environment.

Microfactories with Multiprocessing Equipment for IC Manufacturing

Krishna C. Saraswat
Department of Electrical Engineering
Stanford University

At Stanford, we are developing concepts of a *microfactory*, an alternative approach to IC fabrication, which may offer more economical small scale production, higher flexibility to accommodate many products on several processes, and faster turnaround to hasten product innovation. This approach is based on a new generation of less expensive multifunctional equipment implemented in a smaller flexible factory with extensive use of computer integrated manufacturing (CIM). The new type of multiprocessing equipment quickly process one semiconductor wafer at a time, performs several process steps in-situ in contrast to the conventional alternative of slowly processing many wafers simultaneously and one step per equipment. The process equipment is also modular, with common mechanical and electronic interfaces. Such modularization and standardization is expected to decrease the amount and expense of equiment that must be purchased for existing fabs to upgrade to new generations of technology. Extensive use of CIM for specification, monitoring, control, and information management should make switching between processes faster and more reliable, should increase the ease by which large numbers of different products could simultaneously be routed and tracked through the factory, and maximize equipment untilization.

Economic modeling suggests that small factories (less than a million chips a month) technology would cost about half of their conventional counterparts at similar capacities. (However, this advantage would probably diminish for higher volume factories.) In addition, modeling and initial program results suggest the manufacturing time required to produce the chip will decrease by a factor of three to ten, depending on the chip technology and the degree of loading and product variety in the factory. Finally, initial program results suggest that the new control strategies will make it possible to economically design and manufacture a much wider variety of chips simultaneously in a factory.

Abstract
NATO Workshop on in situ Processing
27 April - 1 May 1992
Viana Do Castel, Portugal

Submission Deadline: 21 February

A NOVEL TWO-STEP, LOW-TEMPERATURE, PLASMA-ASSISTED SURFACE OXIDATION/THIN FILM DEPOSITION PROCESS FOR FABRICATING DEVICE-QUALITY SiO_2/Si HETEROSTRUCTURES

G. Lucovsky, Department of Physics, and Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695-8202

In the conventional high temperature thermal oxidation, and rapid thermal oxidation, RTO, processes used to fabricate commercial SiO_2/Si structures at ~850-1050°C, the SiO_2/Si interface and bulk-oxide are formed at the *same time*. We have developed a novel low-temperature plasma-assisted process for formation of SiO_2/Si structures at 200-300°C that separately controls and optimizes the properties of the SiO_2/Si interface, and the bulk SiO_2, by *separating interface formation from bulk-oxide deposition*. After an ex-situ RCA clean with a final HF dip, the Si substrate is inserted into a UHV-compatible multichamber system, heated to 200-300°C, and oxidized by exposure to O-atoms from a remote O_2/He plasma. An SiO_2 film, typically 100-150Å thick, is then deposited onto the oxidized Si surface using remote PECVD at 200°C, with SiH_4 and N_2O is the source gases. The oxidation step: i) removes residual C contamination from the Si surface; ii) prevents N incorporation at the interface from the O-atom source gas, N_2O; and iii) forms an oxide layer ~6Å thick, and an SiO_2/Si interface with a trap density, D_{it}, of about 1-2x10^{10}cm^{-2}eV^{-1}. The interface properties remain unchanged for oxide deposition temperatures between 200 and 300°C; however, the bulk properties of the oxide, e.g., minimization of mobile charge, are optimized for a deposition temperature of ~200°C.

Insitu Process Control Opportunities for a Deep UV Lithography Cluster

S. Holmes, J. Sturtevant
IBM Corporation
Essex Junction, Vermont 05452, USA

We have developed a deep UV (DUV) lithography process for the production of 16-Mb DRAM chips at 400-500-nm groundrules. Several features of this process are suitable for insitu process control methods. In particular, image size is a strong function of post-expose bake time and temperature. Changes in thickness, index of refraction, or other physical properties of the resist during this bake may provide a means of monitoring image formation or overlay. We have a prototype for monitoring image formation at this step. This system would regulate image size through modifications to the bake time. Post-expose bake temperature is the most critical parameter for image size, so control at this point is important. In addition, variations in earlier process steps that affect image size can be compensated for at the bake operation. These variables could include substrate reflectivity, reticle image size, exposure, and resist sensitivity. During the bake, the wafer is stationary and unobscured by process chemicals, unlike the develop operation; this enhances signal strength and repeatability.

Other opportunities for the implementation of insitu lithography controls could include overlay, film thickness, and reflectivity measurements. Currently, these parameters are measured on separate equipment, which substantially increases cycle time. These measurements are handled either as tool set-up operations conducted on a specific schedule, or are included as routine operating procedures for each product job. Automated data handling capabilities can improve tool and product monitoring, and allow for automatic feedback of product characterization data. While this can improve a process capability, it does not address the need for reduced cycle time and real time process control that can be achieved by clustering and insitu measurement systems.

UV treatment of native oxides with silane : A demonstration of its possibility and its usefulness as an in-situ preliminary treatment in the case of dielectric deposition of SiO_2.

C.Licoppe, C.Meriadec, J.M.Moison, F.Houzay and A.C.Papadopoulo

Laboratoire de Bagneux, C.N.E.T.
196 avenue Henri Ravera, B.P.107, 92225, Bagneux, France.

We show that silane, even if inert under ultraviolet irradiation in the 170-200 nm range, photoreacts with hydrated surfaces. This mechanism where ultraviolet absorption occurs on the surface occurs in traditional UVCVD, though it is a minoritory reaction pathway, and may offer a way towards controlled layer-by-layer photodeposition of silica. We also show that a similar reaction occurs on an InP native oxide surface, causing a reduction of these oxides and the photo-induced formation of an ultrathin dielectric layer on these films, with covalent In-Si-O bonds. In a parallel experiment, It is shown how standard UVCVD of silica on III-V semiconductors at high deposition rates exhibits a transitory deposition regime, making necessary preliminary in-situ treatments compatible with the deposition process. The effects of the silane + UV preparation are eventually discussed in cathodoluminescence experiments.

Real-Time Process Monitors for *In-Situ* Processing

S. R. J. Brueck
Center for High Technology Materials
University of New Mexico
Albuquerque, NM 87131

The advent of single-wafer processing and cluster tools is placing increasing demands on real-time monitors for process control. This is especially true for rapid-thermal processes and for plasma processes. A variety of real-time process monitors including: chemometrics for deposition and etching processes, moiré temperature measurement, and scatterometry for monitoring submicron CDs will be presented. Chemometrics is a powerful statistical multivariate analysis procedure that has been applied to film deposition, to plasma emission and absorption, and to other metrology problems for semiconductor processing. Moiré temperature measurement has been demonstrated with a resolution of less than ±0.5°C over the entire temperature range (-150 to 1200°C) of interest for Si processing. Finally, scatterometry provides a rapid, remote, noncontact monitor of submicron structures, which can be applied to many *in-situ* applications.

Partial support provided by SRC/SEMATECH

FUTURE ISSUES WITH LITHOGRAPHY

by Prof. R. A. Lawes

Lithography for CMOS memory devices (DRAMs) dominates the requirements for any major development of equipment. The resolution of the smallest features, the very large amounts of data and the accuracy with which, individual features must be located already place severe demands on requirement design. Over the next few years even more extreme demands will be made and lithography may have to be significantly improved from current performance.

The major manufacturers in Europe have already decided that the next generation of commercial semiconductors eg 64 Mb DRAM will be manufactured by conventional optical systems operating at high numerical aperture and at the wavelength of the Krypton Fluoride excimer laser ie λ = 248nm. Such systems should be capable of resolving linewidths down to 0.35μm.

A key issue for lithography must soon be addressed, that is to identify the techniques capable of resolving 0.25μm linewidths for the 256 Mb DRAM and 0.15μm linewidths for the 1Gb DRAM.

Several technical questions will have to be answered:

- will improvements to excimer lasers and suitable conventional optics be adequate?
- will phase shift masks with excimer lasers provide the necessary improvements of resolution and depth of focus?
- will x-ray lithography at long last realise its potential?
- can e-beam or other mask-making techniques keep up with the resolution, the mass of data and feature placement accuracy required?

The talk will provide an overview of the likely directions of lithography development and attempt to answer the questions.

PULSED LASER DEPOSITION OF SOME II-VI ALLOYS

A. Aydınlı
Bilkent University, Department of Physics
Bilkent, Ankara, 06533, Turkey

and

A. Compaan
University of Toledo
Department of Physics and Astronomy
Toledo, Ohio, 43606 U.S.A

Pulsed laser deposition (PLD) of materials is a growing field with applications to many systems. With many materials, however, particulate formation is a major problem due to splashing of molten droplets or "ablation" of solid clusters from the target. For the case of II-VI semiconductors, we have found that careful selection of laser power density and appropriate rastering of the beam could reduce particulate formation to a negligible level even with the use of pressed target. In this work, we have deposited a number of II-VI semiconductors and their alloys, using a XeCl laser, from pressed targets onto various substrates in high vacuum. The ternaries of ZnTe and ZnSe as well as ZnTe and CdTe were studied in detail. We determined the optimum growth temperatures and deposition rates for growth of optical quality films. X-ray diffraction, optical absorption, energy dispersive x-ray analysis and Raman scattering were used to characterize these films for grain size and orientation, optical gap and alloy effects on phonon bands.

In-situ Processing of GaAs with Photons: Method, Mechanisms and Viability

Richard B. Jackman
University College London, Electronic and Electrical Engineering, Torrington Place, London, WC1E 7JE, UK

IW Boyd (*Electronic and Electrical Engineering, University College London, UK*)
J Eric-Bouree(*Centre National de la Recherche Scientific (CNRS), Meudon, France*),
J Flicstein (*Centre National D'Etudes des Telecommunications (CNET), Bagneux, France*)
M Green (*Electrical Engineering, Imperial College, London, UK*)
B Leon (*Departamento de Fisica Aplicada, University of Vigo, Vigo, Spain*)
WC Sinke (*FOM instituut voor Atoom-en molecuulfysica, Amsterdam, Netherlands*)

The benefits of an *in-situ* processing approach for semiconductor device fabrication should be particularly valuable for GaAs. This material is readily damaged and low quality interfaces can quickly render GaAs devices useless. A processing technology that relies on chemical changes to the GaAs driven by a photon beam may enable the highly damaging effects of many ion and electron beam based processes to be avoided. The localised nature of the photon assisted approach (through the use of patterned or focused sources) is highly compatible with a maskless processing scheme, essential to *in-situ* processing. The use of a single, ultra-high vacuum, environment, as offered by the *in-situ* approach would avoid interfacial contamination. Thus, the combination of these two methodologies may be ideal for GaAs device processing.

The realisation of GaAs photo-assisted *in-situ* chemical processing requires a number of key issues to be addressed, such as the choice of chemical precursor gases (which must not be antagonistic to the UHV system) and the choice of photon source and operating configuration for optimal *all round* processing capability. Of major importance is the achievement of processing steps which result in device quality material and are highly reproducible; this requires the fundamental mechanisms of the processing step to be understood and the process to then be optimised.

This paper will consider these issues with reference to photo-assisted chemical etching, dielectric deposition and metallisation of GaAs. The operating criteria, fundamental mechanisms and ultimate quality of *etching* will be considered in detail. For example, whilst high quality, highly spatially resolved features have been achieved with laser assisted chlorine etching, distinct advantages have been identified in the use more complex precursors in terms of reactivity and surface contamination. The relative merits of this form of beam assisted processing for GaAs will then be contrasted with the potential offered by other forms of beams.

Optical Diagnostic Techniques for Fabrication Process Control

Gabriel M. Crean, P.V. Kelly, M. Murtagh, S. Lynch, J. Beechinor.

National Microelectronics Research Centre, Lee Maltings, Prospect Row, Cork 1, Ireland.

As micro electronic technologies increase in complexity, design rule geometries are reduced. The corresponding sensitivitry of circuit performance to variations in the semiconductor manufacturing process increases. This sensitivity can be translated into poor manufacturing yields resulting in higher production costs. Stringent process tolerances on material parameters such as layer composition and microstructure are therefore necessary for successful microelectronic system manufacture. To ensure that these and other process criteria such as uniformity and reproducibility are satisfied requires on line or in situ process control.

The optimal solution necessitates collaboration between semiconductor technologists, equipment manufacturers and materials characterisation scientists working in multi-disciplinary teams. Within this framework as discussed in this presentation, current research effort is focussed on developing optical diagnostic tools for specific semiconductor process steps. Optical techniques are particularly suited to in situ process control because of their non-invasive nature and their applicability in a wide range of environments, from atmospheric pressure to ultrahigh vacuum (UHV), and in particular, in the technologically important metallorganic vapour phase epitaxy (MOVPE) and wet etch environments. Reflectance techniques such as spectroscopic ellipsometry have been integrated into process control with dramatic increases in the uniformity, thickness and composition tolerances of product materials. In addition, ex situ optical studies can provide a great deal of additional information on the product materials, which can be related back to the process conditions. Examples of this include the measurement of ion implantation profiles, doses, and damage using photoreflectance, and the measurement of layer thicknesses and uniformity in silicon-on-insulator wafers using ellipsometry.

However, this approach requires an analytical strategy which must address the choice of optical probe, equipment configuration, and sophisticated parameter extraction decision trees. Examples of the state-of-the-art in a range of optical diagnostic techniques, and European research programs in this field are presented.

Fast Room-Temperature Growth of SiO_2 Films by Molecular-Layer Dosing*

D. J. Ehrlich and J. Melngailis

Lincoln Laboratory, Massachusetts Institute of Technology,
Lexington, Massachusetts 02173

Abstract

A molecular-layer dosing technique for room-temperature growth of α-SiO_2 thin films has been developed. The process, based on the reaction of H_2O and $SiCl_4$ adsorbates, is catalyzed by the hydrated SiO_2 growth surface and requires a specific surface phase of hydrogen-bonded water. Careful adjustment of the coverage of this last phase is used to moderate continuous or pulsed growth. Thicknesses can be controlled to several-molecular-layer precision; alternatively, fast conformal growth to rates exceeding 100 nm/min can be achieved by slight depression of the substrate temperature below room temperature. Important potential applications are trench filling for VLSI and hermetic ultra-thin layers, for example, for multilayer photoresists. Excimer-laser-induced surface modification has been used to achieve projection-patterned selective-area growth on silicon. This last result relies on the conversion from hydrogen to hydroxyl termination of the initial growth surface.

*This work was sponsored by the Defense Advanced Research Projects Agency and the Air Force Office of Scientific Research.

Flexible Intelligent Microelectronics Manufacturing

Arati Prabhakar
Director, Microelectronics Technology Office
Defense Advanced Research Projects Agency

The current economy-of-scale approach to microelectronics manufacturing is optimized to produce a single part type in large volumes: a state-of-the-art facility today is a $600M, 30,000 wafer/month fab that makes DRAMs exclusively. Both military and commercial needs for integrated circuits, however, demand many part types, many processes, and rapid turnaround for chips with the highest integration level and performance and in any volume. This presentation will outline DARPA's plans to create the tools and methodologies for flexible, intelligent microelectronics manufacturing. Key aspects include:

- modular cluster tools with real-time model-based process control;
- cost-effective lithography;
- contamination-free infrastructure;
- computer-integrated manufacturing (CIM) systems;
- modeling and simulation tools to design tools, processes, and factories.

The development and integration of these technologies will establish the capability to manufacture a large product mix of state-of-the-art chips in varying volumes with week-long turnaround -- a radically new approach to microelectronics manufacturing.

LASER-BASED TOOLS IN IBM's MANUFACTURING LINES

John R. Lankard & Thomas A. Wassick
International Business Machines Corporation
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A primary goal of the computer industry is to reduce the cycle time associated with signal processing. One way of doing this is to shorten the distance the signals have to travel to and from the chip and to other parts of the computer. This translates to increased wiring density in the package, and drives increased process complexity. Tooling requirements also become more challenging and older tools may no longer meet the new product specifications. It then becomes the responsibility of process and tooling engineers to meet the new challenges in designing, building, and testing a completely new tool-set.

Four and a half years ago, IBM introduced three new laser-based processes for the manufacture of the glass ceramic Thermal Conduction Modules used in the recently announced System/390 computers; laser projection ablation of vias in polyimide, laser shorts repair for removal of unwanted metal, and LCVD opens repair for repairing missing metal defects in lines. Ablation and shorts repair are excimer laser based, while the LCVD system uses an argon ion laser. The basis for each of the tools will be discussed, including the rationale for the lasers chosen, the wavelengths used, as well as a discussion of optical materials, beam delivery systems and homogenizers, photomasks, part registration and handling, and laser reliability.

The Thermolytic LCVD of High Purity Gold Tracks from Alkyl (Trialkylphosphine) Gold(I) Complexes.

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We have recently reported[1] LCVD of high purity gold tracks from gaseous alkyl (trialkyl phosphine) gold(I) complexes, $RAuPR'_3$ (R = Et, Me, R′ = Et), at scan speeds of up to 35 μm s^{-1}.

We speculate that the volatility of by-products of the deposition reaction has an important effect upon deposit quality and in order to investigate this further we describe here the thermolytic laser writing of Au from methyl (trimethylphosphine) gold(I), $MeAuPMe_3$. This complex is a white crystalline solid with a melting point of 75°C by DSC. It has a vapour pressure in the mtorr range and in the vapour phase is transparent to frequencies above 300nm.

Thermolytic LCVD of Au was carried out on (100) n-type single crystal silicon with thermally grown oxide layer (3000Å) and other substrates, using the output from an argon ion laser (Coherent Innova 100-10) at 514.5nm. Except for a reduction in base pressure to below 10^{-6} torr, experimental procedures were identical to those employed in deposition from other compounds in this class of precursors, described by us elsewhere[1]. Deposits were grown at a range of scan speeds from 0-200 μm s^{-1} and characterized by SEM, LIMA and scanning profilometry. Deposit conductivities were measured using a picoammeter

The relationship between power density, beam residence time and deposit volume was measured. The threshold power density for deposition under a stationary beam was determined and the effect of beam residence time upon minimum power densities required for the onset of detectable deposition is discussed.

The morphology of the deposited from the onset of detectable nucleation, through to the formation of continuous tracks, was analysed by SEM micrographs of deposits grown at successively increasing power densities. Isolated nucleation sites were evident at or near the threshold power, increasing in number with power density and gradually coalescing into continuous tracks. Changes in deposit morphology with power density and scan speed were observed. These include periodicity in track width and at high power densities the development of "volcano" shaped profiles.

Electrical conductivities within a factor of 2 of bulk gold are reported for the as deposited tracks. These are consistent with deposit purities of better than 99% (LIMA), without the need for a post annealing step. The precursors we have utilised give the lowest resistivities reported to date for gold tracks deposited by LCVD at writing rates of 0-200 $\mu m\ s^{-1}$.

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Application of laser and ion-beam processing in the repair of integrated and hybrid circuits.

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Laser and ion beam processing have been successfully used in the cutting of interconnections, the etching of insulators for via opening and the local deposition of metals and insulators for local repair of integrated and hybrid circuits.

The laser tool is a cw argon laser with the beam focused on the circuit surface to locally increase the temperature. This temperature, which can be very high depending on the laser power, induces an evaporation of the connection material allowing the cutting function. When the circuit is placed in a reactive atmosphere, this high temperature induces a local decomposition of organometallic molecules resulting in the formation of a new metallic interconnection in the circuit. The cutting speed can be very high, whereas, for deposition, a finite chemical reaction rate generally limits the writing speed of the laser beam to below 0.1 mm/s.

The ion beam tool consists of a high-energy ion beam also focused on the circuit surface. This ion beam is capable of ablating insulator layers on the circuit surface and, therefore, of inducing local etching of very small areas (above 1 μm^2) for via openings. In the case where the insulator is covered or replaced by an adsorbed layer of organometallic molecules, such as $W(CO)_6$, the ion beam decomposes the adsorbed molecules. A local deposition of tungsten occurs, thus allowing the formation of a short metallic interconnection between two conducting layers or two neighboring conducting lines.

In our presentation, we will describe the mechanisms involved in both techniques and their application in the repair of the hybrid and integrated circuits that are under development in the present-day electronics industry.

EXCIMER LASER MICRO MACHINING

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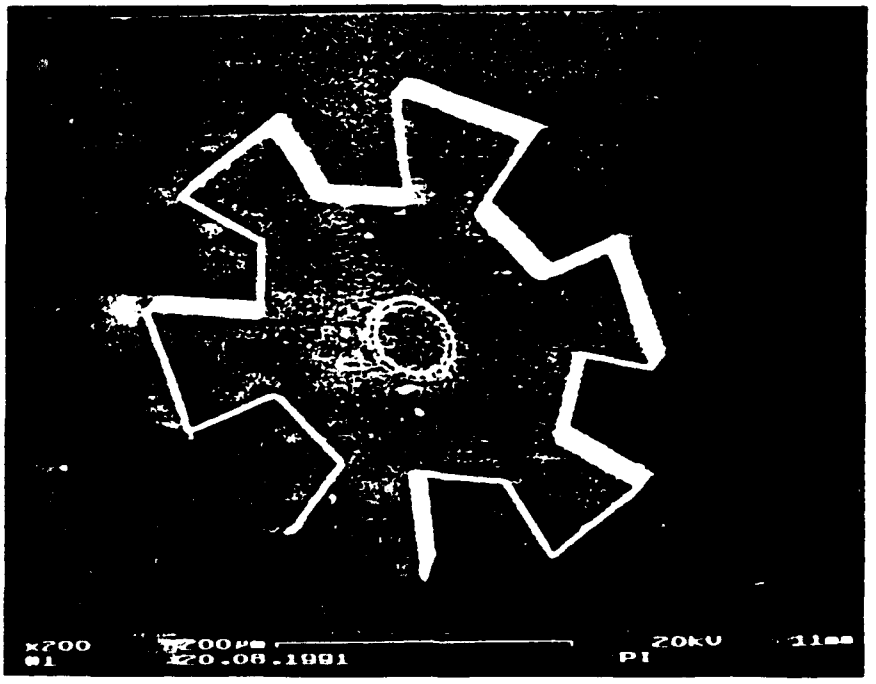
Abstract submitted to

NATO ASI Workshop on in situ Processing
27 April - 1 May, 1992 in Viana Do Castelo, Portugal

Conventional techniques to produce microsized components are restricted to specific material classes and they require a number of processing steps. Excimer laser micro machining is a one step process and not restricted to specific materials. Surface modification is achieved by laser ablation. Complex planar structures are generated either by mask projection or by laser writing using a focused laser spot and moving the sample computer controlled. In that way the process can be optimized for either high production rate or flexibility, respectively. Three dimensional structures can be produced by using a combination of variable masks, sample moving and energy fluence adjustment.

Machining of several materials like polymers, metals and ceramics has been tested. Micrometer resolution can be achieved in case of polymers, whereas high definition processing of metals is complicated by the occuring surface melting. The excimer laser wavelength (193nm, 248nm, 308nm, 351nm) can be selected according to material and processing requirements. The energy fluence has to be tuned in a way that on the one hand material removal takes place at a sufficient ablation rate, but that on the other hand a loss of mask image definition by plasma formation is prevented.

Excimer laser fabricated micro cog-wheel:



A 5 Year Projection for Commercialization of Beam Technologies in Circuit Engineering and Testing

by

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ABSTRACT

Fierce competition in the semiconductor industry continues to drive the reduction in device analysis cycle time in circuit engineering applications including design debug, failure analysis and manufacturing yield analysis. These are all highly financially leveraged applications. The rewards to the organization that executes successfully are market share and profitability while the penalty for failure is often oblivion. This market reality drives vendors to provide tools on the leading of technology that make device analysis efficient.

As integrated circuit geometries continue to shrink well beyond the practical limit for optical microscopy-based solutions for circuit engineering applications, the requirement for charged particle beam-based tools continues to grow. This basic requirement is exacerbated by the parallel explosion in packing density and circuit complexity making essential the integration of these tools with the CAD & CAE design environment.

This review will cover:

Integrated circuit technology trends
Applications requirements today and in the future
Electron-Beam Probing & Focused Ion Beam technology
Technology limitations today and in the future

Commercial Systems today
Market Size
Geographical trends
Market Players and the continuing industry shake out

E-beam probing technology futures
Focused Ion Beam Technology futures
Competing technologies
Dual/Column beam systems

NATO ADVANCED STUDY INSTITUTE

WORKSHOP ON IN SITU PROCESSING
THE PHYSICS AND CHEMISTRY OF SURFACE MODIFICATION

Abstract

"Laser Materials Processing by Ablation and Deposition"

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The exposure of materials surfaces to directed beams of energetic radiation can - at suitable fluences - lead to spatially controlled modification of surface and subsurface properties. With optical (laser[1]) radiation, the energy can be coupled in through high density environments, therefore the surface can be in contact to a gas at high pressure, a liquid or solid film. Spatial control to sub µm dimensions, and energy pulse durations and timing in the femtosecond regime are available.

Laser ablation has proven to be a practical tool for patterned sub µm accuracy removal from polymers and other materials. The advantage of optical control of the absorption coefficient (incubation[2]) and the benefits of ultrashort pulses[3,4] for precise control of the ablation process will be summarized.

Patterned metallization of surfaces can be generated by laser (thermal) chemical deposition from suitable precusors. Trialkylamine-alanes $(Alkyl)_3N \cdot AlH_3$ have shown to allow spatially controlled deposition of aluminum at substrate temperatures exceeding only about 100° C, therefore heat sensitive polymer substrates like polycarbonate and polyimide can be metallized by laser direct write from the gaseous precursor environment. In addition, with suitable catalytic and patterned activation of the surface, high rate Al metallization from gaseous[5] or liquid[6] Al-precursors can be achieved.

The role of laser mass spectroscopic techniques including ultrashort laser pulses[7] for in-situ processing diagnostics will be discussed. Free standing metal micro-objects[8] can be fabricated using a combination of laser deposition/ablation techniques.

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Laser Ablation Deposition of Thin Films

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The use of pulsed lasers to vaporize or 'ablate' materials and to deposit these as thin films on suitable substrates has been studied for many years [1]. For some materials such as II-VI semiconductors (eg. CdTe) quite remarkable progress has been made using this technique, with capabilities that are comparable to molecular-beam-epitaxy for growing relatively complex low dimensional structures [2].

This field has received renewed impetus from the discovery of high temperature superconductors [2] and the need for high quality films of materials such as $YBa_2Cu_3O_7$ in basic physics studies and device applications. Of a variety of techniques for growing these films [4] laser ablation deposition [5] has emerged as a particularly simple and versatile method and has been studied by many groups [6]. Its virtue resides in achieving stoichiometric transfer from complex compound targets using a clean and flexible photon beam processing source. This work has in turn stimulated effort on other materials which are required in thin film form for device applications [7].

In this presentation a brief review will be given of the pulsed laser ablation-deposition technique with emphasis on superconductors and of the underlying physics involved in the ablation and material transport steps. The capabilities of this method which include in situ processing, controlled film orientation, and multilevel growth for device applications will also be covered.

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Laser Ablation Deposition of Thin Films and Surface Analysis by STM/AFM

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Deposition of thin films of superconductive $Y_1Ba_2Cu_3O_{7-x}$, ferromagnetic $Pb(Zr_{1-x}Ti_x)O_3$, La-doped C_{60} and pure C_{60} has been performed with XeCl excimer laser radiation at 308 nm.

Diagnostic of the ablation process is accomplished in-situ by monitoring, from different regions of the plume, the fluorescence emission [1] through an optical time of flight system and the ion yield [2] through a time of flight mass spectrometer.

Surface analysis of the films deposited by laser ablation is made at atomic scale by a home made scanning microscope [3] with electronic tunneling/atomic force interchangeable heads.

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Laser Material Interaction for Atomic Layer Processing

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There exists experimental evidence which suggests that low fluence (0.1-10 mJ/cm^2) laser/surface irradiation (LFLI) induces the species desorption via an electronic excitation mechanism. Measurements show a wavelength dependence in the product populations, KE distributions which are non thermal, and product yields commensurate with the MBE process. Furthermore, there is evidence which suggests that atomic layer-by-layer pealing may be possible with the LFLI process. These results lay the foundation for an advanced laser/material processing technique whereby wavelength tuned lasers are used to grow superlattice structures via atom-by-atom deposition. In addition, the same laser beams are used to modify, on the atomic scale, the growth surface by species-specific desorption. We will present the experimental results which lead to the conclusions above along with a conceptual analysis for such a facility.

A modified plasma source for controlled layer thickness synthesis in laser pulse vapour deposition (LPVD)

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The conventional thin film deposition equipment of LPVD has been modified for the preparation of nm-layer stacks of uniform thickness at reduced target/substrate separation. Therefore, during thin film deposition a substrate translation is preferred instead of the usual rotation technique. The target regime has been changed:

a) a planar target is replaced by a cylindrical target that offers a curved surface to the impinging laser beam and
b) the usual two-dimensional motion of the emitting surface is modified to a continuous adjustment of the actual laser ablation zone at the same spatial location throughout the entire target motion.

Then, the curved target is passing this point and causes a continuous change of the surface normal direction of the emitting area and thus a motion of the plume symmetry axis across a well defined solid angle. The emission characteristics of the plasma source can now be computer controlled and tailored via the stepper motor driven manipulator for the desired layer thickness profile across an extented substrate. Thus e.g. homogeneous film thickness is obtained even for lower target/substrate distances and an appropriate deposition rate can be maintained.

First applications of the equipment will be explained and compared with typical results of the conventional technique.

TOTAL PRESSURE AND SUBSTRATE TEMPERATURE DEPENDENCE OF THE CO_2 LASER-INDUCED CVD OF SILICA FILMS

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Low-temperature silicon oxide films have been successfully grown from SiH_4-N_2O mixtures using a cw-CO_2 laser tuned at 10.6 μm in parallel configuration. The reaction is thermally driven by the gas heating as consequence of the multiple succesive photon absorption by silane molecules followed by the energy redistribution in the mixture by intermolecular collisions. The study of both the total gas pressure and the substrate temperature dependences in the stoichiometric regime (i.e., for reactant mixture ratios $[N_2O]/[SiH_4]$ higher than 25) has demonstrated that the peak temperature reached in the gas phase controls the deposition rate, revealing that the process is led by homogeneous reactions. The gas temperature distribution has been calculated by means of a simple steady-state energy balance in the gas phase which explains very well the experimental growth rates as well as the properties of the obtained films.

LASER INDUCED DEPOSITION OF ALUMINUM FROM TRIMETHYLAMINE-ALANE.

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Up to now, the conventional CVD as well as the laser-induced deposition of aluminum have employed the readily available trialkylaluminum precursors (trimethylaluminum and triisobutylaluminum). Unfortunately both of these compounds decompose to carbon-contaminated films, due to the formation of reactive alkyl radicals.

We report in this work the use of a novel hydride adduct precursor, namely trimethylamine-alane (TMAAH), as a good source for laser-induced deposition of high purity aluminum films. This precursor is a white crystalline powder at room temperature with a high vapor pressure (2 Torr).

Aluminum deposition on GaAs and Si_3N_4 has been achieved by a pyrolytic decomposition of TMAAH using a cw Ar^+ laser (λ = 514 nm). 20 μm wide lines have been drawn under laser-induced local temperatures lower than 250°C at writing speeds as high as 50 μm/s. The deposition kinetics will be presented. The composition of the deposits has been evaluated by SEM+EDX analyses. Furthermore the line resistivity has been measured using aluminum test patterns on GaAs wafers deposited by sputerring.

TMAAH molecules have been also decomposed by a purely photolytic process at wafer surface temperatures as low as 40°C, using a frequency doubled cw Ar^+ laser (λ = 257 nm). The decomposition leads to the formation of alumina aggregates and the deposition rates are very small (100 Å/s).

VACUUM LITHOGRAPHY FOR IN-SITU NANOSTRUCTURE FABRICATION USING FINELY FOCUSED ION BEAMS AND MOLECULAR BEAM EPITAXY

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Processing of semiconductor devices within a high vacuum or controlled ambient environment has received much attention over the past few years. The motivations for in-situ processing include avoidance of contamination or oxidation in the atmosphere, improved device yields, and process simplification. The realization of in-situ processing ranges from cluster tool processing for silicon VLSI devices to all ultra high vacuum processing compatible with molecular beam epitaxy for III-V optoelectronic devices. This paper will review our work in-situ processing methods with particular emphasis on combinations of fine scale patterning and crystal growth in the III-V materials. A vacuum lithography technique using a finely focused ion beam , dry etching, and molecular beam epitaxy will be described in the context of patterning and overgrowth of InP-based semiconductor materials. A variation of the vacuum lithography technique has also been used for patterning and MOMBE selective area growth. Examples of devices and nanostructures fabricated by these techniques will be presented. The capabilities and limitations of focused ion beam vacuum lithography will be described in the talk.

Direct E-beam deposition of 3 dimensional nanometer-scale Atomic Force Microscope sensors

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Abstract

In recent years, there has been a rapid advance in the development of scanning tunneling microscope(STM) and atomic force microscope(AFM) for various fundamental physical studies. As the semiconductor device dimensions shrink from micron to submicron level, the development of STM and AFM tools for technological applications is going to play an increasingly important role in the various stages of device development i.e. for process monitoring, reliability testing and device fabrication. Currently, the techniques used to fabricate the AFM probe tips result in tip shapes which are not reproducible. This is clearly not adequate for engineering applications where specific and reproducible AFM tip shapes on a nanometer scale are desirable. For example, for metrology of submicron trench structures with a depth of 1 μm or more, nanometer-scale tip shapes with high aspect ratio will be required.

High resolution direct E-beam deposition where the adsorbed organometallic molecules are decomposed under electron beam irradiation, provides a unique capability for the fabrication of high aspect ratio, nanometer-scale AFM tip structures. This is demonstrated in Fig.1 where an E-beam fabricated AFM tip grown on top of a silicon cantilever structure is shown. The tip dimension is $\simeq$ 0.1 μm in diameter and 4 μm in height. This AFM force sensor(Si cantilever and tip) has been successfully used for the first time to profile a 1 μm deep silicon trench with a trench opening as small as 0.36 μm.(Fig.2)

Experiments had also been carried out to study various parameters which affect the growth behavior of a self-supporting nanostructure from a nanostructure support. These results have recently enabled the fabrication of complex, self-supporting three dimensional nanostructures which opens up a whole new category of sensors and transducers. In this talk, results on application of the E-beam fabricated AFM sensors for high resolution metrology will be described. Examples of various 3 dimensional E-beam fabricated nano-mechanical devices and their potential applications will also be discussed.

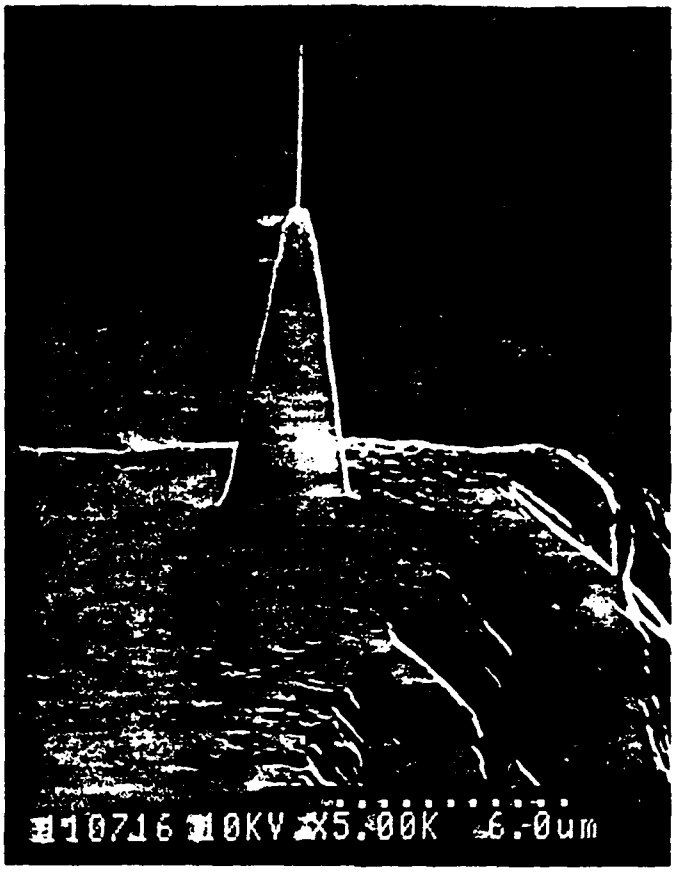

Fig.1 An Example which shows a high aspect ratio nanometer scale atomic force tip deposited on an integrated tip on a Si cantilever.

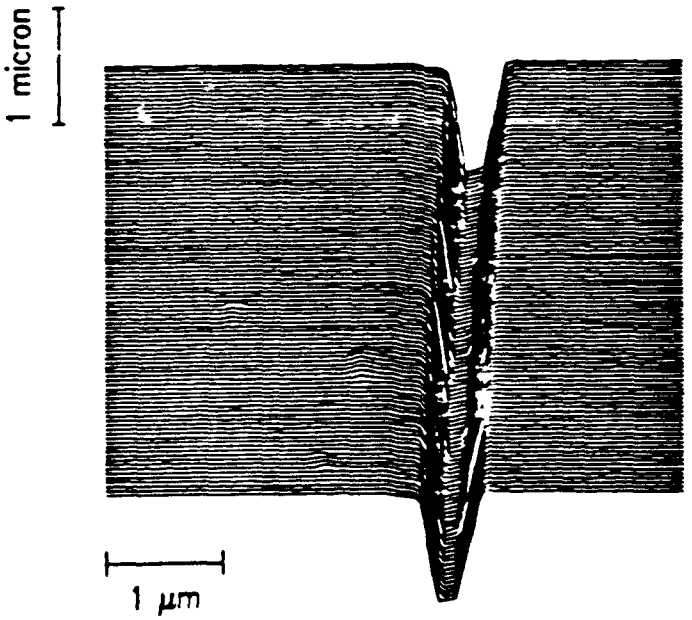

Fig.2 AFM profile of a Si trench with ≃ 0.3 μm opening and 1 μm deep obtained using an E-beam fabricated tip.

Optimizing the Performance of a Focused Ion Beam System

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A high resolution focused ion beam (FIB) is an excellent tool for modifying a surface on a micrometer scale because the focused beam can be moved with a few nanometers precision over an area of many tens of micrometers while it removes material gently, by sputtering or adds material by causing the decomposition of an appropriate gas. Consequently, the FIB makes possible a micromachining system that can work on a micrometer level.

If the current density J(r) of a focused beam were uniform it would be possible to predict the outcome of a machining process with confidence. Unfortunately, the current density profile J(r) is a complicated function of aberrations of the ion focusing system (see Figure 1). As a result, the morphology of a machined surface is difficult to predict and it is often necessary to work by trial and error to obtain a desired end feature. While there have been attempts to eliminate the aberrations of the focusing systems by resorting to mixed electric-magnetic quadrupole optics, the results to date have not been very successful because these systems are so complicated. In the meanwhile, it is necessary to find a way to optimize the performance of existing systems by producing the optimum J(r) of which the system is capable.

We have found that a careful analysis of ion trajectories indicates how one can obtain the optimum current density distribution for micromachining. Once an optical system has been analyzed, it is a simple matter to make the necessary adjustments in its operation so as to be able to obtain the best performance the optics are capable of.

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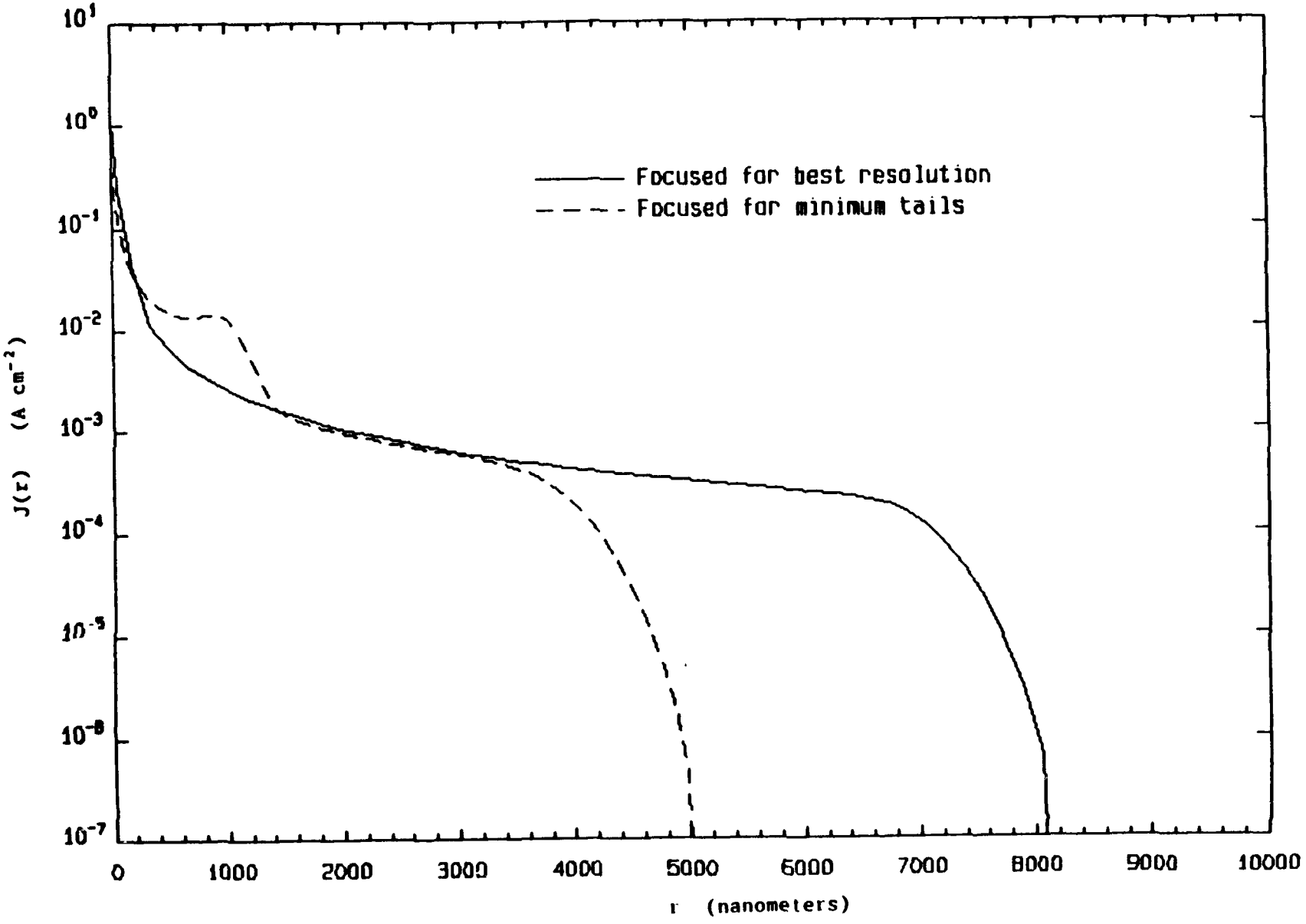

Figure 1. The calculated current density profile J(r) for an ion beam system at two different states of focus.

In-situ EB lithography of GaAs toward nanometer-scale structures.

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UHV in-situ processing is a key-technology for the fabrication of nanometer-scale structures such as quantum wires and/or dots. We have developed a new in-situ electron beam (EB) lithography for GaAs patterning, using an oxidized layer of a few monolayer thick as a resist film and a mask for the subsequent Cl_2 gas etching. The durability of the oxide layer to Cl_2 gas is modified by EB irradiation, making laterally fine patterning possible.

For this "in-situ EB lithography", UHV environment is indispensable because the thin oxide layer must be formed on the contamination-free, well-controlled surface. To avoid surface degradation, furthermore, the oxide layer can be removed by heating the wafer under arsenic pressure, and overgrowth on it can be performed successively. These processes are performed using originally developed multichamber system comprising seven chambers for loading, sample exchanging, sample pre-heating, MBE, surface oxidization, etching, and surface analysis.

Low energy focused ion beam system and in-situ processing

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We have been developing low energy (0.05-25keV) focused ion beam (LEFIB) system and investigating various maskless processing including ion beam assisted etching, digital etching and deposition for in-situ microfabrication. Our system consists of a liquid metal alloy ion source, condenser and objective lenses, an E×B mass filter, an astigmator and a beam scanner and uses a retarding field technique. The system is connected with molecular beam epitaxy system and is used for selective doping and etching of GaAs/GaAlAs heterostructures.

Up to now, etching characteristics of and the effect of residual damage in GaAs has been investigated. An etching yield of ~10 atoms/ion for 200eV Ga FIB irradiation in Cl_2 atmosphere at room temperature was obtained. It was observed that at this low energy, band-edge photoluminescence intensity at 83.1nm decreased only by 20% after the etching and full recovery was obtained after annealing at 600°C for 10 min. Further reduction of damage was achieved by etching in Cl_2 atmosphere after irradiating Ga LEFIB to remove thin native oxides which act as an etching mask. This technique is also advantageous as in-situ patterning technique in the respect that a low dose of ~10^{15}/cm^2 is enough to form 50-100nm thick, etched groves. Residual damage was also measured by DLTS technique for irradiation at a dose required for selective doping for 2DEG. It was observed that for 100eV Ga LEFIB, defects (~10^{16}/cm^2) induced by the irradiation decreased below detection limit (<1×10^{15}/cm^2) after annealing at 400°C for 10 min.

All these observations indicate that LEFIB is effective to minimize damage and promising for in-situ processing.

Nanofabrication using STM Tip

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A scanning tunneling microscope (STM) tip has been used to locally modify surface layers of materials. Hillock and/or hole formation as a function of pulse amplitude, pulse width of applied voltage, and tunneling-gap width was studied in various atmospheres such as air, vacuum, and chloride gas. The influence of voltage pulses on STM tips during nanofabrication was investigated. Problems arising from STM processing such as location of the STM tip in a required place were overcome by combining the STM with a SEM system. An *in-situ* nanofabrication system using STM and SEM is discussed.

NANOSECOND THERMAL PROCESSING: A LASER BASED ULTRA-SHALLOW DOPING PROCESS FOR SILICON TECHNOLOGY

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Continued performance increases in silicon ULSI depend on both lateral and vertical dimensional scaling of conventional devices, such as MOS and bipolar transistors. To achieve these goals development of new device structures along with advanced processing technologies is required. The critical, lateral dimensions of devices are predicted to decrease below 300 nm during the next five years, reaching 100 nm in the late nineties. These dramatic decreases in dimensions result primarily from advances in lithography (*eg.* *X*-ray, phase-contrast *uv*) and dry etchant patterning technologies.

Equally important, however, is the scaling of *vertical* dimensions. Up to now progress here has not been as dramatic, since present dopant incorporation mechanisms (*eg.* ion implantation and diffusion) have proven adequate for past designs. In this talk, we introduce the concept of nanosecond thermal processing (NTP), a new approach to transient thermal processing technology. This technique uses a pulsed *uv*-laser to perform selective, die-by-die annealing, doping and diffusion on a *nanosecond* time scale. The use of rapid thermal cycles ($< 1\mu s$) and precise control of impurity profiles, inherent to NTP, addresses several of the important vertical scaling problems faced for bipolar and MOS devices.

We have implemented several processes which are based on NTP: *i*) dopant incorporation, accomplished by simply placing the wafer in a dopant gas cell during irradiation, *ii*) selective annealing and redistribution of previously deposited dopant layers, and *iii*) diffusion from both doped and undoped silicides. Unlike other laser processes which use small beams to individually write device structures, the NTP process uses a large area, homogeneous beam to process wafers on a die-by-die basis, similar to a modern lithography stepper. The process uses conventional masking techniques and can be easily inserted into a modern semiconductor manufacturing line with little or no change in the process flow.

Details of the process, simulation of the experimental melt-diffusion results along with successful *state-of-the-art* device results are presented.

IN SITU DRY CLEANING TECHNIQUES FOR CRITICAL SURFACES

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In situ controlled atmosphere processing requires the development of new, dry removal methods for organics, metals and particulates. The ideal cleaning techniques would utilize gas phase reactants to produce gas phase products which could be easily removed from the system.

For the removal of organics, the uv/ozone process shows promise. The basic premise is the use of ozone to oxidize organic materials, including remaining photoresist, to CO_2 and H_2O and the corresponding S and N oxides as appropriate. The advantages and limitations of this procedure will be discussed briefly.

The current "killer" defect for submicron scale semiconductor manufacturing is particulate contamination. Traditionally, particles have been removed using wet processes such as ultrasonic and megasonic cleaning. Several new dry processes have recently been developed, including bombarding the surface with a "snow" of a normally gaseous material such as Ar or CO_2 and laser irradiation of a similarly condensable material which has been adsorbed under and around the particle. Particle removal for the latter process occurs via explosive evaporation of the adsorbed liquid, thus making microrockets of the particles [1]. In our initial experiments in laser assisted particle removal (LAPR), the adsorbed energy transfer medium is water and the laser is a TEA CO_2 at 10.6 and 9.6 μm. Under these conditions, polystyrene and alumina particles deposited on Si substrates can be efficiently removed [2]. The measured thresholds of LAPR are independent of particle size for diameters of 1 - 10 μm but are a function of the absorption coefficient of the energy transfer medium. We conclude, therefore, that absorption of the laser energy into the energy transfer medium is the dominant factor under our experimental conditions. At energy densities greater than twice the particle removal threshold, a shock wave is generated. An analysis of the shock wave as a function laser energy density and water deposition conditions will be reported.

References:

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Abstract submitted to " Workshop on In Situ Processing "
The Physics and Technology of Surface Modification, 27 April- 1 May 1992
NATO Advanced Study Institute
Viana Do Castelo (Portugal)

UV-Induced Removal of Hydrogen , Hydroxyl and Water Groups in Silica Thin Films Photodeposited at Low Temperatures

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Silicon-based dielectric films prepared at low temperature by UVCVD contain a significant amount of defects (-H,-OH, H_2O), impeding their use in sequential deposition on fragile substrates, for examples in multilayer structures (dielectric mirrors ,dielectric waveguides, etc.). We show here how such films can be repaired in situ at room temperature, with the use of high luminance energetic UV lamp irradiation.
Silica films were prepared at low temperature , by irradiation of a nitrogen : oxygen : silane gaseous mixture (50 : 20 : 1) with a low pressure mercury lamp (185 nm). Thin films with thicknesses between 250 and 1300 A° and a refraction index of 1.45 were obtained at a rate of 1000 A°/ min. Deposited films were subsequently in situ exposed to a new pulsed Krypton lamp with an average UV (170 - 250 nm) luminance of 42 mW/ cm^2 sr.Hz. Processing of photo-deposited silica to this powerful UV lamp, while monitoring with FTIR spectroscopy, is shown to cause full removal of Si-H bonds. The overall photoinduced reaction, which occurs at low temperature (0-200 °C) is independent of the film thickness and does not lead to the creation of dangling bonds as shown by electron spin resonance (ESR) measurements. While direct photolysis of Si-H is ruled out, the reaction path involves, surface and bulk, hydroxyl and water groups consumption. This "UV annealing" technique may be extended to the in situ treatment of many other hydrated surfaces.

LASER-ASSISTED ETCHING OF SILICON BY CHLORINE: PROGRESS OF A MECHANISTIC STUDY

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Basic mechanisms involved in laser etching of silicon by chlorine are studied in a high vacuum apparatus. The most salient and useful features of the experimental setup are: a pulsed injection of the active gas, which allows kinetic studies of the absorption/desorption processes, elimination of gas-phase photoreactions and in-situ diagnostics, a time-of-flight mass spectrometer, providing mass and kinetic energy distributions of the etch products and time resolved reflectivity measurement used to monitor the superficial fusion of Si.

The recent results will be described. The main conclusions are:

1) laser etching has been studied with various pulsed lasers (XeCl, KrF, N2, doubled and tripled YAG): whereas no significant wavelength-related effect was observed, contrary to previous reports, the practical etching results are extremely diverse, due to laser beam properties.

2) the etch rate becomes significant at the same laser fluence which induces superficial fusion of Si.

3) a significant amount of Cl is incorporated into the molten layer, and several laser shots whithout Cl_2 dosing are required to desorb it.

4) the melting of 100-200 nm allows the redistribution of implanted dopants through liquid-phase diffusion. For the Boron dopant, etching selectivity leads to a large increase of the superficial B doping, and the creation of a sharp doping level concentration.

Periodic Submicron Dot Structures on Semiconductor Substrates Fabricated by Laser-Induced Surface Electromagnetic Wave Etching

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Abstract

Recently, fabrication of periodic dot structures has been studied, since these structures are attractive for quantum well box devices. However, it has been extremely difficult to fabricate the structures, since the size of the dots is required to minimize less than 0.1 μm and many dots are needed to locate periodically. In laser annealing, laser CVD and laser etching, fabrication of periodic structures with periods shorter than the laser wavelengths has been demonstrated. These periodic structures are defined by the spatial modulation of optical intensity resulting from the interference between the incident laser light and the surface electromagnetic waves(SEWs). By controlling the fabrication spatially, we obtained the periodic submicron dot structures on InP and GaAs substrates.

The experimental setup was the holographic exposure for direct etching of the semiconductors using the frequency-tripled and -quadrupled Nd:YAG laser (Quantel, YG681). Laser output power was about 0.1-1 W and pulsewidth was approximately 5 ns. The laser beam was polarized perpendicularly to the plane of incidence (s-polarization) so that SEW gratings could be formed perpendicular to holographic gratings and then interfered on the semiconductor substrates. Atmospheric-pressure He-diluted CH_3Br mixture (1%CH_3Br/99%He) was used as an effective etching gas.

As one of experimental results, periodic dot structures of less than 0.2 μm in diameter was fabricated by photochemical etching of InP(100). The incident angle (θ) of the frequency-tripled Nd:YAG laser was set at 19°. Longitudinal broad lines were grooves of holographic gratings and horizontal narrow lines were grooves of the SEW gratings. The interval of holographic gratings was 567 nm and the interval of the SEW gratings was 379 nm.

The period depends on incident angle and wavelength of lasers. Therefore, dot structures with shorter periods are obtainable if a shorter-wavelength laser is used. The frequency-quadruppled Nd:YAG laser was also used. Dot structures with different periods on InP and GaAs will be presented.

Kinetic Energy and Mass Distributions of Ablated Species formed during Pulsed Laser Deposition

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Pulsed Laser Deposition (PLD) is an important technique for the stoichiometric deposition of a variety of complex materials systems such as high Tc superconductors, ferroelectrics, x-ray optical materials and magnetic thin films. An incident laser pulse on the surface of a bulk target of several nanoseconds duration causes ablation which may be directed to a heated substrate, thus resulting in thin film deposition. Parameters such as the kinetic energy (KE) distribution, ionisation state and mass distribution of the ablated species are likely to have implications for optimisation of the thin film growth process.

A cylindrical mirror analyser/mass spectrometer (VG Quadrupoles) able to measure mass fragments from 0-600 amu and energies from 0-500eV has been used to characterise the ablated species. Several target materials have been studied e.g. carbon, metals (Fe,Cu,Pb,Ta), oxides (CeO_2), high Tc superconductors ($YBa_2Cu_3O_7$, Bi-Sr-Ca-Cu-O) and ferroelectrics (PZT). Lasers used for the ablation process were an excimer (KrF 248nm, ArF 193nm) and a frequency doubled Nd:YAG laser (532nm) source. We report here results showing KE distributions of species as a function of laser fluence. Close to the ablation threshold detected ion energies in the range 0-15eV were measured. By increasing the laser fluence the KE range of the ablated species expands to 0-80eV. These results are considered with reference to the current theories of PLD.

SYNCHROTRON RADIATION AS AN IN-SITU MONITORING AND PROCESS TOOL -- WALTER LOWE, AT&T BELL LABORATORIES, MURRAY HILL, NJ

Within the past 20 years x-ray sources have become "more available" for different types of applications other than analytical and characterization studies. Accompanying this increased availability has been a tremendous improvement in source characteristics. Source brightness, for instance, has increased by 5 orders of magnitude with the new third generation synchrotron radiation sources. One of the current interests in x-rays produced by synchrotron radiation is the processing of materials, the most notable example being x-ray lithography. Aside from lithography there are many other areas of processing where x-rays can be employed. Synchrotron radiation can be used for in-situ characterization, monitoring and process control. Processes that require rapid changes in temperature to cause modifications at the atomic scale is an important example where x-ray monitoring could be used. For instance rapid thermal processing is used to fabricate most semiconductor devices and is employed in the growth process of the base material. Synchrotron radiation will be discussed in the above context, as an in-situ monitoring/processing tool. I will give an overview of the production of x-rays by synchrotron radiation and describe materials processing at the beamline endstations. Looking to the future, an important question is how synchrotron radiation tools will be used and where are the hurdles to be overcome?

REAL TIME PLUME DIAGNOSTICS DURING LASER ABLATION IN AN OXYGEN ATMOSPHERE

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Laser deposition of thin films is already acknowledged as a powerful method to produce complex oxide thin films. The inclusion of oxygen in the deposition chamber has been shown to be important to achieve the desired stoichiometry avoiding "ex-situ" post-deposition treatments. It has been also shown that the composition, excitation state and velocity of the species in the plume play an important role in the film properties. Many spectroscopies have been used in order to determine the nature and kinetics of the plume species, including absorption, emission and mass spectrometry.

In this work, we report results on the plume kinetics in the presence of a background oxygen pressure (up to 10 mbar) and we will relate them to the properties of films grown by UV laser ablation. To characterize the plume kinetics we analyze "in situ" the light emitted by the plume with time - space - spectral resolution. To characterize the film growth we monitor in real time the film reflectivity. Complementary "ex situ" analysis of film stoichiometry, optical and structural properties are performed by means of ion related techniques (RBS and NRA), spectroscopic ellipsometry and TEM respectively. Most of the results to be presented are related to the growth of Ge and Ge oxide films. The use of a single component target with no oxygen content facilitates the analysis of the influence of an oxygen background pressure in the film stoichiometry.

The results show that the velocity of both neutral and ionized species is in the range of 10^6 cm/s and does not depend on the oxygen pressure. In addition, there is no evidence of reactions in the vapour phase as the plume expands or of the presence of molecules in the plume . The results allow us to conclude that the reactions which yield the formation of oxide films takes place at the substrate, most probably in the solid phase. Some preliminary results related to multiphoton excitation experiments performed in order to analyze the role of non excited species together with the isotope contribution will be also discussed.

Laser and Remote Plasma-enhanced Low Temperature Si and Si-Ge Epitaxy

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This talk will review recent progress in very low temperature (150-450 C) Si and Si-Ge epitaxy using laser beam and remote plasma excitation in ultra high vacuum systems, which opens up possibilities not only in terms of growing structures with abrupt doping transitions and heterointerfaces but also in terms of potentially new thermally-mismatched materials combinations. Photodissociation of disilane by an ArF excimer laser operating at 193 nm has been used to grow Si epitaxial films free of stacking faults and dislocation loop densities below TEM detection limits. A growth kinetic model for the process based on the generation of $SiHSiH_3$ has been developed.

In related work, remote r-f plasma-enhanced chemical vapor deposition, where the substrate as well as the reactant silane/germane gases are not directly exposed to the glow discharge, has been used to grow Si epitaxial films as well as Si-Ge quantum wells and superlattices. Key to the process is an *in situ* remote H plasma surface cleaning step prior to epitaxy. Detailed microstructural characterization of these films using RHEED, TEM, SIMS and Nomarski microscopy will be presented. Results of *in situ* doping of these films during low temperature epitaxy, and electrical characterization using Hall effect measurements, as well as low temperature (<450 C) device fabrication on these films will be discussed. The future potential of such technologies will be assessed.

Dynamics of YO monoxide formation during YBCO laser ablation

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Actually, laser ablation is gaining increasing interest as a viable method in thin-films technology. Processing control and modelling of the laser ablation depend on the understanding of the basic physics and chemistry inside the laser induced plasma (LIP) plume.

In this paper, we present results of time-of-flight measurements by optical and ion probe methods. We used superconducting YBCO targets and two kinds of excitation : nanosecond (XeCl excimer laser) and picosecond (YAG laser, pulse duration $\tau = 35$ ps at FWHM) ones. The last type of excitation allows to reduce the temperature dispersion of the ejected species, so that the expansion dynamics can be observed more properly than under nanosecond one.

In the nanosecond excitation range, all emitting species including BaO and CuO oxides show one velocity component. The picosecond excitation, however, allows to observe the more complex velocity distributions of the ejected species. The broadening and shift to the higher energy of these distributions are governed by the kinetics of electron-ion recombination. Under both excitations, a peculiar feature was observed from time-of-flight spectra (TOF) of the YO molecule. These TOF spectra show two velocity components : a slow one with unusual properties and a fast one with expansion velocity corresponding to an average velocity of the monoatomic species. A formation mechanism of the low velocity YO population is discussed in terms of the chemical reaction of Y with oxygen. The result of this reaction is a strongly excited state of the YO molecule. An emission following the excitation allows energy conservation and subsequent stabilization of the molecule via radiative cooling. The proposed reaction scheme requires a strong velocity selection which involves a reaction of the rapid oxygen population with low energetic (low velocity) yttrium atoms and vice-versa.

Ion emission studies of pulsed laser deposition

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In pulsed laser deposition (PLD) of thin films it is widely held that the energetic ion content of the laser ablation plume has important effects on the nature of the film growth. We have used an ion collector to study the variation with laser fluence of the magnitude and energy distribution of the ion flux emitted from metal and high-Tc superconductor materials, and compared the results with theoretical models of ion acceleration. In the same experiment a quartz crystal was used to measure the variation of the deposition rate. The fraction of deposition occuring via ionised material was estimated.

We have also examined the effect of causing an electrical discharge in the laser ablation plasma plume and investigated how the deposition rate and production of particulate material depends on the energy in the discharge.

Optical Characterisation of Metal Contaminations in Silicon via Femtosecond Laser Pulses

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Failure of highly integrated semiconductor devices because of metal contaminations has become a severe problem in VLSI-Technology. Conventionally, observation of metal precipitates is performed by wet etching of the silicon surface leaving etch pits at contaminated regions that are investigated with a microscope. Besides its destructiveness it is a major disadvantage of this technique that it does not allow the determination of the metal precipitate itself. Recently, it has been demonstrated that cw-modulated reflectance techniques can be applied successfully to nondestructive monitoring of metal impurities in silicon, although no direct information about electrical activity can be gained. We use *transient reflectivity measurements* as a novel technique to characterize metal impurities in silicon. Transient reflectivity measurements are performed in a pump/probe configuration in which reflectivity changes caused by an intense femtosecond excitation pulse are measured by a second delayed pulse. Measurements are performed with 50 fs pulses at 2 eV from a colliding-pulse modelocked ring dye laser. In order to determine the spatial position of metal contaminations, the system operates in a time integrating mode where reflectivity changes are mainly governed by the lattice temperature. Contaminated regions are dectected via the change in heat conducting properties. The time-resolved measurement scheme then allows a sensitive observation of the photoexcited carrier dynamic giving direct information about free carrier lifetimes and transport properties. Fig. 1 shows the transient reflectivity changes of various intentionally contaminated silicon samples and a non-contaminated reference sample. The relaxation of photinduced carries in the contaminated samples occures much faster than in non-contaminated silicon. Furthermore, relaxation times τ_r can be devided into two different timescales related to the concentration of the metal impurities. The slow relaxation on a timescale of several hundred picoseconds can be ascribed to the capture of photoinduced carriers into deep defect states that are generated by the metal impurities. The fast relaxation time of a few hundred femtoseconds cannot be explained by this effect. We assume that this fast relaxation

of photoexcited carriers is caused by an ultrafast transport in the electric field of a metal/semiconductor contact. This assumption is supported by estimations of the carrier dynamics using the Schottky-Modell and transient reflectivity changes of metalsilicides.

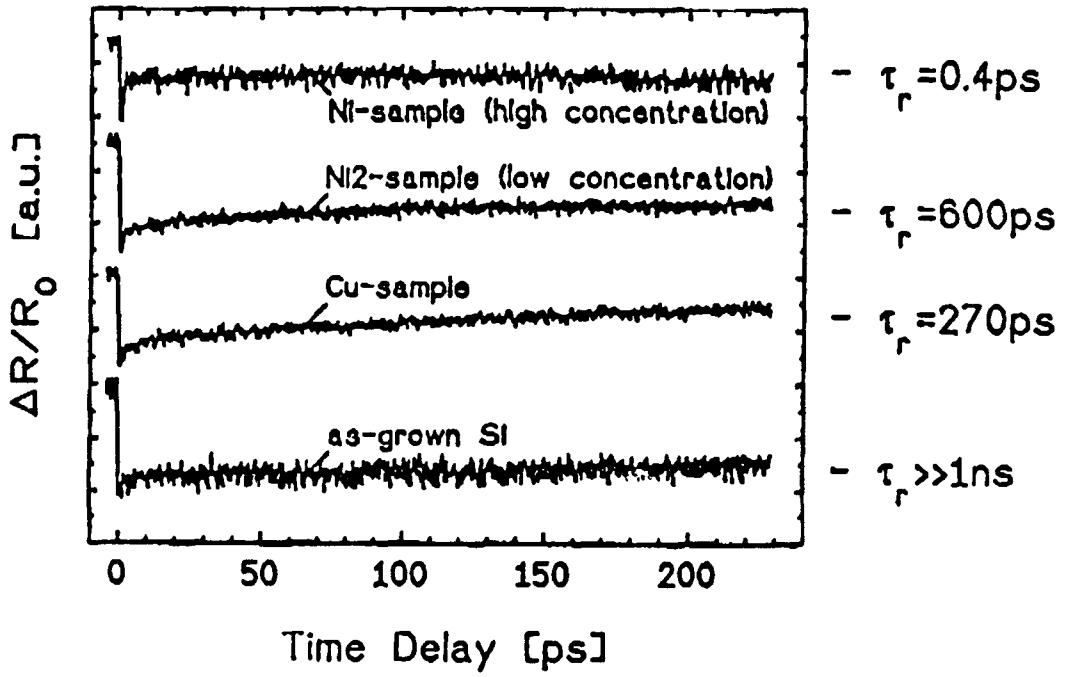

Fig. 1: Transient reflectivity changes of contaminated silicon in comparison to non-contaminated silicon

Applications of local laser CVD in microelectronics

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Abstract

ICs interconnection layers can be locally modified by inducing chemical reactions on the circuit surface using a tightly focused laser beam. Metals and insulators can be either etched away or deposited within the laser spot, i.e. on few square micrometres areas.

This paper presents the tests performed on devices from major European IC manufacturers and illustrates the potential applications of laser CVD in microelectronics. A full repair process is described and characterization results for each process step will be provided.

FOCUSED ION BEAMS FOR DEVICE MODIFICATION

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With shrinking device geometries, more layers of metalization and increasing design complexities sub-micron FIB device modifications, as a part of the IC development process, are becoming more common. Liquid Metal Ion Source and electrostatic optics technologies have matured and lead to the rapid development of systems dedicated to device modification. This, in turn, has lead to the development of applications and techniques that exploit the imaging, milling and localized deposition capabilities of these systems. The results of work done in our lab, in cooperation with a number of device manufacturers, using a FIB system will be shown along with a brief discussion of the methods employed.

LASER ASSISTED DEPOSITION OF TUNGSTEN LINES AND COLUMNS ON SILICON OXYNITRIDE: PROCESS CHARACTERIZATION AND APPLICATIONS

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Laser direct writing of tungsten through the reduction reaction of tungsten hexafluoride (WF_6) by hydrogen is investigated. Tungsten is deposited on substrates of 0.6 μm thick plasma CVD silicon oxynitride (SiO_xN_y) grown on c-Si. We emphasis the study on the problems of process control and possible applications. The influence of various parameters such as laser power (p) and gas composition on line morphology and profile is presented.

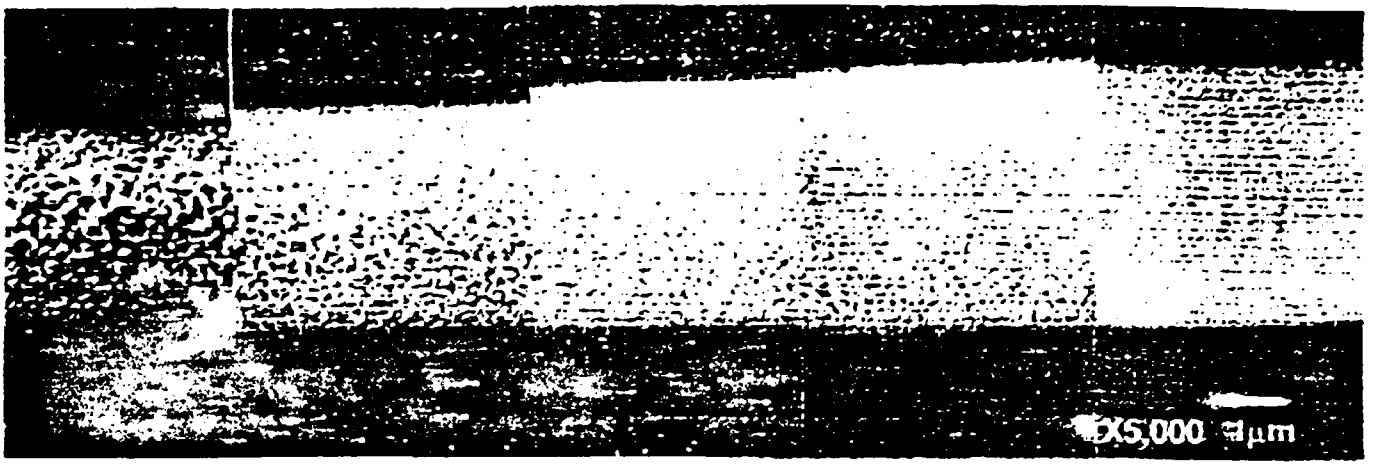
The laser direct writing deposition system is based on an Ar^+ laser operated at 488 nm. The beam is focused on the substrate using either a 0.15 or 0.31 NA objective. The writing is done by moving the chamber with computer controlled X-Y stages which have a resolution of 0.1 μm and a maximum speed of 100 μm/s.

Typical deposited lines have linewidths of 2.5 to 15 μm and line thicknesses of 0.1 to 2 μm. They show a good adhesion to the substrate as determined by the scotch tape test. The composition is measured by Auger Electron Spectroscopy (AES). After a short surface cleaning by Ar sputtering, no fluorine or other contaminants are observed in the detection limit of AES (1 at %). Depending on deposition conditions, resistivities range from 13 to 25 μΩ-cm, which corresponds to two to four times the bulk resistivity of tungsten (5.6 μΩ-cm).

Figure 1 shows the increase of linewidth and the important variations of grain size and line morphology as a function of hydrogen pressure $P(H_2)$. In addition to these visible variations, line thickness decreases as $P(H_2)$ increases. This suggests that although if H_2 participates in the surface chemical reactions, excess of H_2 acts as a buffer gas.

Leaving the laser beam stationary on one point, tungsten columns instead of lines can also be deposited. Columns 25 μm in diameter and 80 to 100 μm high were realized. Figure 2 shows the sharp tip obtained by this method. Application of these deposited W columns for the realization of three dimensions contacts for the fabrication of various sensors is under investigation.

Application of laser deposition of W for the microsurgery of electronic circuits having a thick passivation layer (> 0.5 μm) was realized in combination with another laser system used for opening via holes by excimer laser ablation.



i ii iii iv v

Figure 1. SEM micrographs of lines deposited in different H_2 partial pressures, i = 100 Torr; ii = 200 Torr; iii = 300 Torr; iv = 400 Torr; v = 500 Torr. $P(WF_6)$ = 10 Torr, p = 0.35 W, NA = 0.31, v = 100 μm.

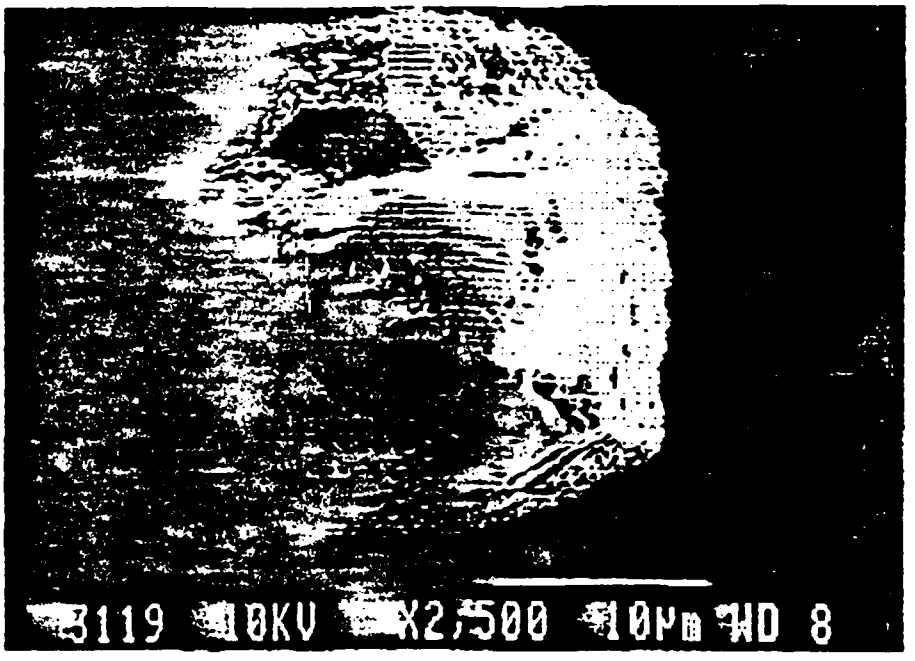


Figure 2. SEM micrograph showing the sharp tip of a 100 μm high W column made by laser processing. $P(WF_6)$ = 10 Torr, $P(H_2)$ = 100 Torr, NA = 0.15, p = 0.25 W

Laser direct writing of gold conductors from metallo-organic inks

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Abstract

The use of metallo-organic (MO) inks in laser direct-writing of metal conductors represents an interesting alternative to other better investigated but more complex or expensive processes, like laser deposition from gas-phase precursors. One of its main advantages is that no process chamber or vacuum equipment is required, since the process is performed in air. The substrate can be held in the same environment where the laser head operates, removing the geometrical constraints generated by the presence of a reaction cell, one or more windows and the precursor supply system. Furthermore, no handling of dangerous chemicals is involved.

As far as we know, a process leading to good quality micron-sized geometries has never been discussed in detail. In addition, previously reported processes often seemed to be poorly controllable, due to the self-propagating nature of the reaction: this would lead to feature dimensions much larger than the spot size and to the formation of a pronounced periodic structure [1].

Our study has been aimed at developing a simple and relatively inexpensive laser-writing technique for gold deposition. We have used readily available gold bearing MO inks, normally used in screen printing applications. While not specifically designed for laser-writing, these inks have led to good quality gold conductors at a much lower cost than specific ones.

The experimental setup consists basically of an Ar^+ ion laser, a fiber-optic beam delivery system and focusing optics. The substrate holder is mounted on computer controlled XY non-stepping translation stages. After proper dilution, the MO ink is spun on the substrate and soft-baked on a hot plate to remove the solvents. After laser-writing, the unexposed ink is washed off in an ultrasonic bath of organic solvents.

While it is relatively easy to obtain an adhering opaque film - useful, for instance, in photolithographic mask repair - deposition of good conductors turns out to be critically dependent on several experimental parameters. In particular, the initial MO film

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[1] M.E. Gross, G.J. Fisanick, P.K. Gallagher, K.J. Schnoes, and M.D. Fennell, Appl. Phys. Lett. 47 (9), 923 (1985).

thickness, laser power, scan speed and prebake procedures, all influenced the quality of the resulting gold film.

Fig. 1 shows data on width and resistivity of gold lines obtained at a scan speed of 5 μm/s and at different incident laser powers. The silicon substrate is coated with 300 nm SiO_2 and 1.6 μm of ink (Engelhard T18002X). After processing, the substrate is baked at 450 °C for 45 minutes. Within the shown range of parameters, the quality of deposited films is rather independent of irradiation intensity. At higher powers the quality deteriorates due to the ablation of the MO film.

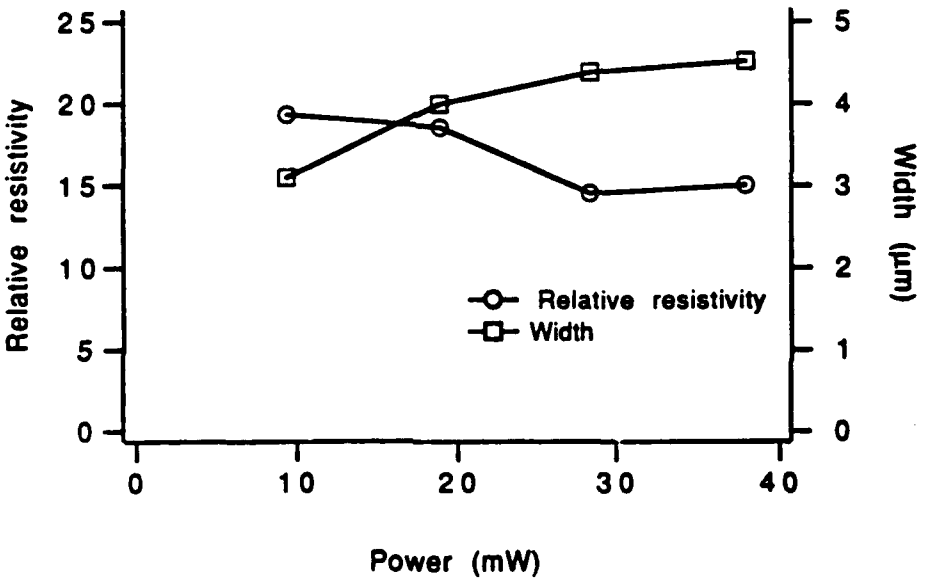

Fig. 1 Data on gold lines written at 5 μm/s with a 1/e spot size of about 2.2 μm (10X, N.A.=0.25 objective). Laser wavelength is 514 nm. Resistivity is relative to bulk gold (2.44 μΩ·cm).

A characterization study is presented in which the behaviour of different commercial MO inks is investigated and an understanding of the process dynamics is attempted. Details on the full procedure are also given, together with data on the quality of the results obtained.

This work has been partially supported by "Progetto Finalizzato Tecnologie Elettroottiche" of the Italian National Research Council.

LASER AND THERMAL PROCESSING FOR Ti:$LiNbO_3$ WAVEGUIDES FABRICATION

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Lithium niobate is known to be an excellent material for integrated optical devices development. One important application of this material is the making on the basis of $LiNbO_3$ single crystal of either planar or channel optical waveguides.

The most common method of formation of these waveguides is titanium diffusion from the surface into the depth of lithium niobate single crystal. During heating however unwanted scattering centers arise leading to the increase of propagation losses in the guide. For this reason research on new technologies arises.

An investigation of direct laser in-diffusion of Ti into lithium niobate single crystals was started in (1), where a ruby laser has proved to be a succesful technique for titanium diffusion into the lithium niobate, and the optimal regime of irradiation was experimentally found. However comparatively shallow Ti-doped layers were formed by means of laser treatment, of an insufficient thickness to make optical waveguides.

In this paper an extension of the previous investigation is reported where a series of Ti-coated $LiNbO_3$ single crystal samples was subjected to Q-switched ruby laser irradiation in different regimes: either light energy density in a single pulse or a number of laser pulses were used, and after the treatment some samples were heated in a furnace for 3 hours at 960 C. The Ti profile measurements were carried out by SIMS method.

(1) M. Bertolotti, M. Rossi, A. Ferrari, V. Craciun, I. Mihailescu, G. N. Mikhailova, Anurada Dhaul, R. Chander, in pubblication on J. Appl. Phys.

ArF laser CVD silicon oxide films tailored by tuning gas-phase parameters.

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ArF excimer laser-induced CVD of silicon oxide thin films from SiH_4 and N_2O precursors using Ar as a buffer gas offers unique possibilities to tailor the properties of the films deposited by changing the N_2O/SiH_4 ratio and the total pressure.

Adding oxidant precursor to the gas mixture, Fourier Transform Infrared analysis (FTIR), ellipsometry and Rutherford Backscattering (RBS) measurements show very wellan increasing film oxidation from suboxide films (n=2.0, ν_{Si-O} = 1040 cm^{-1}, $FWHM_{Si-O}$ = 130 cm^{-1}) to stoichiometric silica (n=1.46, ν_{Si-O} = 1065 cm^{-1}, $FWHM_{Si-O}$ = 75 cm^{-1}) for N_2O/SiH_4 ratios higher than 8. Fora fixed gas mixture and laser beam-to-substrate distance as well, growth rate, composition and density of the films can be varied easily in a wide range not available previously by only tuning the total pressure.

Ceramic thin films deposited on Si(100) by laser ablation. Application as buffer layer for $YBa_2Cu_3O_7$ films.

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ABSTRACT

Ceramic thin films of yttria-stabilized zirconia (YSZ), $SrTiO_3$ (STO) and CeO_2 have been deposited on Si(100) substrates by laser ablation. The films have been characterized by x-ray diffractometry, field emission scanning electron microscopy and secondary ion mass spectrometry. The effects of the oxygen partial pressure during the deposition and the substrate temperature were studied. All the films have preferential orientation: (h00) and (hh0) for STO and (hhh) for CeO_2 and YSZ. The films show a low density of particulates and a very smooth surface. SIMS profiles indicate a low interdiffusion between film and silicon. One of the applications of these materials is their use as buffer layer for the growth of YBCO on silicon. Because both materials are highly reactive, it is necessary to put a barrier between YBCO and silicon. In this sense we used the ceramic films previously deposited, in order to obtain superconducting YBCO films. The deposited YBCO films present good superconducting properties with zero resistance at temperatures between 80 and 85 K.

DIODE LASER INDUCED CHEMICAL VAPOR DEPOSITION OF WSi_x ON TiN FROM WF_6 AND SiH_4

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We have developed a compact and inexpensive laser direct writing system, based on the 796 nm radiation of a 1 W cw GaAlAs diode laser array, for the deposition of tungsten silicides. The laser beam is collimated with a 0.5 NA objective and the ellipticity is reduced with a 4:1 anamorphic prism pair. The collimated beam is directed in a microscope and focused with a 25X (0.31 NA) long working distance objective. The efficiency of the optical system is 55%, yielding up to 550 mW at the substrate. The TiN substrates (100 nm of reactively sputtered TiN on 800 nm SiO_2 on a silicon wafer) are placed in a stainless steel reaction chamber closed by a fused silica window. Line formation is achieved by moving the reaction with computer controlled XY stages which have a 0.1 μm spatial resolution. Lines are written at speeds ranging from 2 to 100 μm/s in the direction parallel to the long axis of the spot. Since it has been shown that SiH_4 can be used to obtain a low temperature reduction of WF_6 [1], such a process seems appropriate for deposition with a diode laser. However, the initiation temperature of that reaction depends strongly on the gas mixture. We present here the diode laser induced deposition of WSi_x on TiN from a mixture of WF_6, SiH_4 and Ar. The substrate is at room temperature during the experiment.

We have already presented preliminary results on the deposition in a static mode where the reaction cell is filled to the desired pressure [2]. We focus here on the deposition in a dynamic mode where the different gases are kept flowing. Figure 1 shows a scanning electron micrograph of a typical WSi_x line on TiN, written at 100 μm/s, using a laser power of 360 mW at the substrate. The total pressure in the reaction cell is 8.9 Torr and the flows f of WF_6, SiH_4 and Ar are respectively 1, 3 and 50 sccm.

Figure 2 shows the line thickness as a function of laser power and Ar proportion of the gas mixture. The WF_6 and SiH_4 flows are kept constant at 1 and 3 sccm respectively while f(Ar) = 50 and 100 sccm. Increasing the amount of Ar in the gas mixture reduces the thickness of the deposit but improves process control and adhesion. Depending on laser power and gas mixture, the linewidth varies from 3.5 to 15 μm. Reproducible and well controlled growth is obtained with a mixture of 1 sccm WF_6, 3 sccm SiH_4 and 50 to 150 sccm Ar.

Auger Electron Spectroscopy analysis indicates that no fluorine is incorporated in the WSi_x film within the limit of detection. Aside from surface contamination, due to air

exposure, no carbon, nitrogen or oxygen are detected in the bulk of the deposited metal. The W/Si ratio is uniform in the bulk and estimated to be between 0.9 and 1.4 when the flows of WF_6 and SiH_4 are 1 and 3 sccm.

[1] J.G. Black, S.P. Doran, M. Rothschild, D.J. Ehrlich, Appl. Phys. Lett. 56, 1072 (1990).
[2] P. Desjardins, R. Izquierdo, M. Meunier, Mat. Res. Soc. Meeting, Symposium B, Boston, November 1991 (to be published).

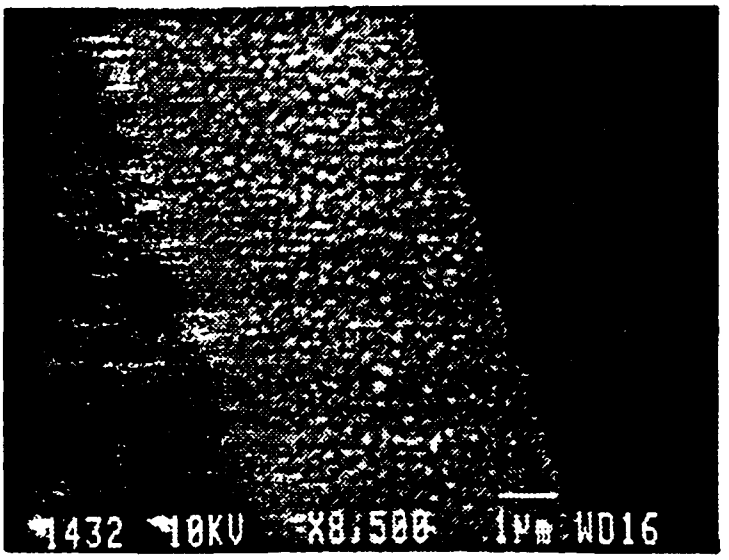

Figure 1. Scanning electron micrograph of a diode-laser-deposited WSi_x line on TiN. Gas flows : f(WF_6) = 1.0 sccm, f(SiH_4) = 3.0 sccm, f(Ar) = 50 sccm, total pressure = 8.9 Torr, laser power = 360 mW, writing speed = 100 µm/s.

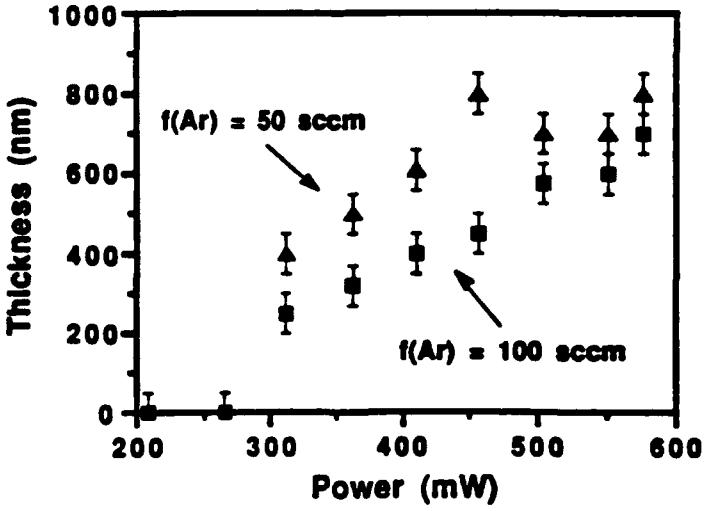

Figure 2. Thickness of laser deposited lines as a function of diode laser power at the substrate. Gas flows : f(SiH_4) = 3.0 sccm, f(WF_6) = 1.0 sccm, f(Ar) = 50 and 100 sccm, total pressure = 8.9 and 12.3 Torr, writing speed v = 100 µm/s.